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ELECTRICAL HEATING ROD AND METHOD
OF MAKING SAME

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The invention relates to electrical heating rods and a method of making them and is particularly concerned with the cold ends of such rods.

One object of the invention is to provide a rod of increased service life. Another object of the invention is to provide rods which will not stick to the furnace refractories. Another object of the invention is to eliminate weakness at the hot zone-cold end junction. Another object of the invention is to provide a cold end of low electrical resistivity. Another object of the invention is to provide a cold end which can very readily be welded to the section which does the heating. Another object of the invention is to improve the material described in U. S. Letters Patent to Henry Noel Potter, 1,030,327, patented June 25, 1912, for use as the cold end of an electrical heating rod. Another object of the invention is to provide a method of making electrical heating rods which will greatly reduce breakage in manufacture and in testing.

Other objects will be in part obvious or in part pointed out hereinafter.

The invention accordingly consists in the features of construction, combinations of elements, arrangements of parts, and in the several steps or relation and order of each of said steps to one or more of the others thereof, all as will be illustratively described herein and the scope of the application of which will be indicated in the following claims.

As conducive to a quicker understanding of the present invention, it is noted that electrical heating rods, sometimes called bars, have for sometime past been made out of recrystallized silicon carbide which was described by Francis A. J. Fitzgerald in U. S. Letters Patent No. 650,234, patented May 22, 1900. Such bars are used in furnaces where the temperature desired is too high for the successful use of metallic resistor wire under oxidizing conditions. Such recrystallized silicon carbide electrical heating resistor rods have a middle portion (lengthwise) where the ohmic resistance from end to end is reasonably high and where consequently a large portion of the voltage drop occurs; they have cold ends of low resistivity where little voltage drop occurs and, of course, the heat is liberated where the resistivity is high, namely in the middle portion of the rod while the cold ends are cold simply because the ohmic resistance of these cold ends is relatively low. The cold ends of these heating electrical resistor rods have made out of the material described by Potter in the aforementioned patent and which

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he called "carbosilicon" although frequently the "carbosilicon" was modified by adding a small percentage of aluminum to lower the resistivity.

The heating rod in accordance with my invention may be recrystallized silicon carbide over the entire length and it is now known in the art how to make a rod of recrystallized silicon carbide; in fact, the disclosure in the above mentioned Fitzgerald patent is believed to be sufficient. Having made a number of such recrystallized silicon carbide heating rods, I cold end them as follows:

I provide a cold ending crucible which may be a block of graphite desirably having a generally cylindrical shape and having a bore at the axis of the block of about 30% greater diameter than the diameter of the rod to be cold ended. The bore should stop short of one end of the block leaving a bottom to the crucible which should be at least one inch thick. This graphite crucible is placed within an induction heating coil and heated to a temperature of about 2100° C. while containing a quantity of silicon. This temperature could, however, be between 1900° C. and 2600° C. Thus for a crucible 12 inches long having a 3 1/2 inch bore 10 inches long, one-quarter of a pound of silicon will be sufficient and more will not do any harm. The silicon impregnates the pores of the graphite over the entire inside surface of the crucible which prevents loss of silicon during the cold ending process as will now be described.

Having thus produced a lining on the wall and bottom of the crucible it is now ready for the cold ending of rods. I first place in the bottom of the crucible lumps of silicon and a powder of a boride which according to the preferred embodiment of my invention is carbon boride, better known as boron carbide. This can be the variety represented by the formula B₄C or it can be the material which has been referred to in the literature as B₅C. The silicon can be of fine grit size if desired but I find no particular advantage in crushing it up fine and consequently use lumps which will just pass a 10 mesh screen. The boron carbide is preferably a very fine powder preferably finer than 220 grit size.

The rod to be cold ended is placed in the crucible on top of the impregnating mixture and then the crucible is heated to well above the melting point of silicon (1420° C.) and I have found that the top temperature can be from 1800° C. to 2600° C. but that best results are attained within the range of from 2000° C. to 2200° C. With regard to the amount of impreg-

nating mixture, for cold ending 10 inches of a $\frac{3}{4}$ inch diameter rod, .22 pound of mixture will suffice if the rod has a porosity of about 30 volume percent pores which is usually the case. The quantity of silicon and boron carbide absorbed per unit volume depends upon the porosity of the rod which may vary from 15% to 45% by volume. To find out the volume of impregnating material required is consequently a simple calculation based upon the volume to be impregnated times the percentage of porosity, from which the quantity in weight can be readily determined by reference to the specific gravity of the material, but the figure so found should be increased to allow for losses and it does not matter if some is left over. The above figure of .22 pound is about double the amount theoretically required.

The impregnating mixture of silicon and boron carbide penetrates the recrystallized silicon carbide which is porous and forms a cold end which appears to be very dense, the porosity being close to zero. The individual grains of silicon carbide can still be distinguished, however. As soon as the mixture of silicon and boride reaches about 1800° C. it starts to permeate the rod, probably by the capillary attraction of the porous rod for the liquid. Permeation is more rapid and complete as the temperature is raised above 1800° C. The length impregnated is dependent upon the length heated to impregnating temperature which is at least 1800° C. and ought to be at least 1900° C. for good results, provided, of course, that there is enough mixture present. For cold ending the other end of the rod the process is repeated at the other end thereof.

The resistivity of the cold ends thus produced depends upon the percentage of boron relative to the silicon in the mixture as shown in the following table:

Table

Percentage of Boron on the Silicon by Weight	Resistivity in Ohm-Centimeters
0.000	0.02 -0.05
0.078	0.008 -0.010
0.195	0.003 -0.005
0.390	0.002 -0.004
0.780	0.002 -0.004
1.560	0.002 -0.003
3.900	0.0017-0.0030

Heating rods with cold ends having a resistivity of 0.010 and lower are far more useful and desirable than similar heating rods having a higher resistivity so therefore I stipulate a boron addition in percentage on the silicon of at least 0.078%. At the other end of the scale I find that impregnation is more difficult if the boron addition is more than 5% on the silicon so therefore as an upper limit I take 5%. Heating rods made in accordance with this invention maintain their thermal efficiency for a long time. They show no tendency to stick to the furnace refractories whereas rods impregnated with silicon and aluminum have this defect. As will be seen in the table, the cold ends have much lower resistivity than those impregnated with silicon alone.

Among the many advantages of the present invention is the fact that highly satisfactory silicon carbide electrical heating rods can now be made by the welding process, manufacturing separately the middle portion and the cold ends.

This process results in far fewer rejections and breakages in manufacturing than the process of making a long silicon carbide rod and impregnating the ends thereof for the following reason: recrystallized silicon carbide is a brittle material especially the unimpregnated pieces. The longer a brittle article is the greater is the danger of breaking it in handling. Since the cold ends are often each twelve inches long and may be longer it follows that making rods in three pieces instead of in one piece results in making materially shorter lengths. The lengths of the middle portions vary but often are from eight inches to thirty-two inches and usually as long as a cold end for the same rod but usually not more than two or three times the length of a cold end for the same rod. At all events great savings in manufacturing have been achieved by making rods in three pieces instead of in one piece. But the manufacturing of the rods in three pieces when the cold ends were impregnated with the customary silicon-aluminum mixture resulted in breakages at the welds in use for reasons mentioned below. According to this invention such breakages at the welds have now been largely eliminated and thus the manufacturing process no longer results in excessive breakage or rejections and rods according to the invention are far more durable under given conditions than any prior rods known to me.

It has been found that rods having welded cold ends which were impregnated with silicon and aluminum were weak at operating temperatures of about 1300° C. and many rods failed in use. When the cold ends were impregnated with silicon with the boron addition as above described, failure at the welds is rare. The customary silicon-aluminum impregnating mixture contained about 12% of aluminum since less would not give as low a resistivity as desired. This material had a molten phase at temperatures of about 580° C. whereas the present impregnating mixture never has a molten phase until a temperature of about 10° below the melting point of silicon is reached. The melting point of silicon is usually taken to be 1420° C. and it has been found that rods according to the present invention can stand a temperature up to 1400° C. at the junctions whether welded or not.

I may make the cold ends in a separate operation and weld them to the middle portion in accordance with the art disclosed by James Kelleher 1,583,473, patented June 15, 1926. Thus, in the above example, I would take recrystallized silicon carbide rods only 12 inches long and impregnate 10 inches thereof with silicon and boron carbide, then cut off the 2 inch unimpregnated portion. The reason for starting with pieces 12 inches long when cold ends only 10 inches long are wanted is to leave an end projecting from the crucible for easy removal of the rod. Such cold ends can be welded to the ends of what will be the middle portion by the following procedure:

Lengths of recrystallized silicon carbide are cold ended for about half an inch on each end by the use of the same graphite crucible using however only enough mixture to cold end for about half an inch. The exact length of these cold ends is not critical. The ends of these short cold ends are now ground to polar zone spherical surfaces as by means of diamond grinding wheels and the ends of the long cold ends are similarly

ground. For a single rod two of these surfaces are convex and two are concave and of course a convex surface is mated with a concave surface. Zones with bases at about 75° latitude are satisfactory. A paste is now prepared from equal parts by weight of green silicon carbide, carbon black and water which is just sufficient water to make an easily trowelled paste. This welding paste is trowelled onto a ground end of one of the portions to be joined. Now assuming the rod is to be three-quarters of an inch in diameter, I provide a ring of graphite cylindrical inside and out, 1 inch inside diameter and 1½ inch outside diameter and three-quarters of an inch long and mount this between graphite electrodes diametrically opposite to each other so that the axis of the ring is horizontal. I then bring a middle portion and a long cold end together within the ring, either the ground end of the middle portion or the ground end of the cold end having been coated with the aforesaid welding paste and of course it is these ground ends which are brought together within the graphite ring but not touching it, and the junction should be midway of the ring lengthwise. This cold end and middle portion should be held together by spring pressure and the exact pressure is not critical but may be from a few ounces to several pounds. A pressure of two pounds per square inch would be satisfactory in practically any case. Around the junction for about half an inch on each side I now trowel a protective paste of silicon-powder and water. Thin hollow frusto-cones of graphite are placed as shields on the rods and against the graphite ring, one on each side with the large ends against the ring and the small ends are just large enough to clear the rods. The large ends of these shields have a diameter the same as that of the ring. The graphite ring is now heated to 2500° C. by passing electrical current through it via the electrodes and the temperature can be gradually raised by increasing the current at intervals in a total time of five and one-half minutes and then the ring is allowed to cool. As a result of this procedure a cold end is united to a middle portion and of course another cold end is similarly united to the other end of the middle portion.

The weld formed by the above operation is strong and durable. The silicon on the surface of the portions being united appears to react with the oxygen of the air to form a protective film of silica which keeps the silicon in the portions adjacent the weld from running out as it otherwise probably would since the temperature is above the melting point of silicon. I have also found that I can make a good weld using the above procedure and a welding paste consisting of only titanium carbide and water.

The paste of silicon on the rods at the junction where the welds are being formed appears to be of some importance since it keeps the silicon in the rod at and near the junction from distilling off. Even though the temperature at the weld is higher than the melting point of silicon this paste protects the junction and I believe the silicon in this paste oxidizes to produce a protecting sheath in the process.

Another reason why there were many breakages of the rods where lengths of silicon carbide were cold ended rather than having cold ends welded to a middle portion is that the cold ending of a long length of a still longer rod frequently caused the rod to break just beyond the portion being cold ended. This was undoubtedly due to

heat shock on the recrystallized silicon carbide. This does not happen when only about half an inch is cold ended, and when the entire length is cold ended there is no heat shock. When a piece is cold ended to a length just a little shorter than the entire length so as to leave a portion sticking out of the crucible for easy removal of the piece, it does not matter if the projecting portion cracks. So therefore breakage by heat shock, formerly a serious problem, is eliminated or reduced in accordance with the method of my invention and by using the boride addition to the silicon, welds which will fail in service are likewise eliminated or reduced.

Instead of using boron carbide for the boron addition, I can add titanium boride or zirconium boride. The titanium boride may be a compound of the formula TiB_2 or of another formula and the zirconium boride may be of the formula ZrB_2 or of another formula. In any event the resulting resistivity will depend upon the percentage of boron on the silicon as shown in the table. Where the addition to the silicon is titanium boride or zirconium boride the method of impregnation is the same as where the addition is boron carbide and in all cases the impregnating mixture should be heated to a temperature within the range already specified for cold ending. A few seconds at the top temperature suffices to cause the impregnation and the crucible can be quickly heated by induction. However, the crucible can also be heated by passing electric current through it, or in any other desired manner in the case of any of the boride additions. I do not wish to be limited to the type of carbon boride now identified as B_2C since boron carbide having an excess of boron can be used and also boron carbide having free carbon therein can be used. In the final product there is present silicon and a boride selected from the group consisting of carbon, titanium, and zirconium borides. Mixtures of these borides can be used for the addition to the silicon and it is quite satisfactory to have cold ends containing mixtures of carbon, titanium, and zirconium borides. If desired the silicon can be premelted and mixed with the boride to produce an impregnating material of silicon containing the boride which can then be crushed to lumps which will pass a ten inch screen or finer.

I have thus provided a new composition of matter for the cold ends of silicon carbide electrical heating rods and this consists of silicon carbide, silicon and boride selected from the group consisting of carbon, titanium and zirconium borides and mixtures thereof, the percentage of boron on the silicon apart from the silicon in the silicon carbide being between 0.078% and 5%. Since absolute purity of anything has hardly ever been achieved I am not to be held thereto and other elements can be present in my composition provided they are not present in excess of 2% of the total composition and this includes uncombined carbon up to 1%. Carbon may be present when impure boride of carbon is used but will not be present in excess of 1% of the total composition as most of it will combine with the silicon present.

As aforesaid the manufacture of silicon carbide electrical heating rods is a known art so it is not necessary for me to describe it in detail. However, I prefer rods made from high purity silicon carbide which is green in color and the process of manufacture may be to comminute the silicon carbide to small grit sizes, then to mold rods therefrom using a compatible temporary

binder such as sodium silicate, then to heat the rods to recrystallizing temperature. In this process the sodium silicate passes off as a gas during the recrystallization so that the resulting recrystallized rod is sometimes better than 99% pure silicon carbide. Such a rod is preferably one of my starting materials.

The composition of the invention is recrystallized silicon carbide crystals from 55% to 85% by volume, the interstices between the crystals being impregnated with silicon and boride selected from the group consisting of carbon, titanium and zirconium borides and mixtures thereof, the percentage of boron on the silicon apart from the silicon in the silicon carbide being between 0.078% and 5% by weight, total other elements in the composition being not more than 2% and including uncombined carbon up to 1%. The impurities may be partly in the crystals and partly in the impregnant. The method, however, is not limited to any proportion of the mixture of silicon and boride to the recrystallized silicon carbide since the impregnation will occur at all events, provided the material has the percentage of boron on the silicon as defined and the material is raised to 1800° C. or higher.

The electrical heating rod according to this invention has cold ends as fully described and has a middle portion which is recrystallized silicon carbide. While so far as many features of the invention are concerned I am not limited to a particular purity of the crystals or a particular purity of the middle portion as a whole or the presence or absence of other materials such as vitrified clay or graphite etc., I now prefer a middle portion the crystals of which are better than 99% pure silicon carbide and this is usually the green variety. Other material in this middle portion apart from the crystals (except where impregnated) is usually practically nonexistent, for example nothing but traces of dirt or foreign matter down to a fraction of a percent of the total composition.

It will thus be seen that there has been provided by this invention an article, a composition and a process in which the various objects hereinabove set forth together with many thoroughly practical advantages are successfully achieved. As many possible embodiments may be made of the above invention and as many changes might be made in the embodiment set forth, it is to be understood that all matter hereinbefore set forth is to be interpreted as illustrative and not in a limiting sense.

I claim:

1. Method of making cold ends for silicon carbide electrical heating rods which comprises placing a mixture of silicon and boride selected from the group consisting of carbon, titanium and zirconium borides and mixtures thereof adjacent a length of recrystallized silicon carbide and heating the mixture to a top temperature between 1800° C. and 2600° C., the percentage of boron on the silicon by weight in the mixture being between 0.078% and 5%.

2. A composition of matter for the cold ends for silicon carbide electrical heating rods comprising recrystallized silicon carbide crystals from 55% to 85% by volume, the interstices between the crystals being impregnated with silicon and boride selected from the group consisting of carbon, titanium and zirconium borides and mixtures thereof, the percentage of boron on the silicon apart from the silicon in the silicon carbide being between 0.078% and 5% by weight, total other elements in the composition being not more than 2% and including uncombined carbon up to 1%.

3. An electrical heating rod comprising a middle portion which is a length of recrystallized silicon carbide, and cold ends beyond said middle portion comprising silicon carbide crystals from 55% to 85% by volume, the interstices between the crystals in the cold ends being impregnated with silicon and boride selected from the group consisting of carbon, titanium and zirconium borides and mixtures thereof, the percentage of boron on the silicon apart from the silicon in the silicon carbide being between 0.078% and 5% by weight, total other elements in the cold ends being not more than 2% and including uncombined carbon up to 1%.

4. An electrical heating rod as claimed in claim 3 in which the middle portion is 99% silicon carbide SiC in the recrystallized physical state.

5. Method according to claim 1 in which the top temperature is between 2000° C. and 2200° C.

GEORGE R. WATSON.

REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
1,658,334	Holmgren	Feb. 7, 1928
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2,445,296	Wejnarth	July 13, 1948